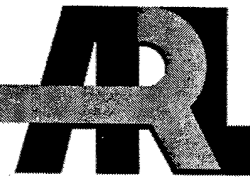


ARMY RESEARCH LABORATORY



Literature Review of Fuel Processing

by Ivan C. Lee and Deryn Chu

ARL-TR-2946

March 2003

Approved for public release; distribution unlimited.

20030610 026

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Citation of manufacturers' or trade names does not constitute an official endorsement or approval of the use thereof.

Army Research Laboratory

Adelphi, MD 20783-1197

ARL-TR-2936

March 2003

Literature Review of Fuel Processing

Ivan C. Lee and Deryn Chu
Sensors and Electron Devices Directorate, ARL

Approved for public release; distribution unlimited.

AQ403-08-2068

INTENTIONALLY LEFT BLANK.

| REPORT DOCUMENTATION PAGE | | | | Form Approved OMB No. 0704-0188 | |
|---|------------------------------------|-------------------------------------|---|--|--|
| <p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p> | | | | | |
| 1. REPORT DATE (DD-MM-YYYY) March 2003 | | 2. REPORT TYPE Review | | 3. DATES COVERED (From - To) NA | |
| 4. TITLE AND SUBTITLE Literature Review of Fuel Processing | | | | 5a. CONTRACT NUMBER | |
| | | | | 5b. GRANT NUMBER | |
| | | | | 5c. PROGRAM ELEMENT NUMBER NA | |
| 6. AUTHOR(S) Ivan C. Lee and Deryn Chu | | | | 5d. PROJECT NUMBER NA | |
| | | | | 5e. TASK NUMBER | |
| | | | | 5f. WORK UNIT NUMBER | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory Attn: AMSRL-SE-DC 2800 Powder Mill Road Adelphi, MD 20783-1197 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-2946 | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory 2800 Powder Mill Road Adelphi, MD 20783-1197 | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) | |
| | | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) | |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited. | | | | | |
| 13. SUPPLEMENTARY NOTES | | | | | |
| 14. ABSTRACT <p>Technology is available for the development of hydrogen-fueled polymer electrolyte membrane (PEM) fuel cell systems of small and intermediate sizes. For the indirect use of organic fuels, such require the development of compact fuel processors to provide high purity hydrogen. Methanol fuel processors are under intensive research and development for that purpose. The associated technical challenges and approaches to their solutions are discussed. Integrated prototype systems of methanol processor and PEM fuel cell systems have been built for portable, mobile, and stationary applications.</p> <p>The additional technical barriers to be overcome for diesel or JP-8 reformers are much more formidable. Carbon and sulfur managements have to be addressed to develop a durable and high-performance logistic fuel reformer for Army applications. In addition, better carbon monoxide removal strategy is necessary, because logistic fuel reformers produce reformat gases containing high carbon monoxide concentration. State-of-the-art logistic fuel reformers are reviewed.</p> | | | | | |
| 15. SUBJECT TERMS Fuel processing, reformation, reforming, reformer, CO removal, methanol, JP-8 diesel | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT UL | 18. NUMBER OF PAGES 34 | 19a. NAME OF RESPONSIBLE PERSON Ivan C. Lee |
| a. REPORT UNCLASSIFIED | b. ABSTRACT UNCLASSIFIED | c. THIS PAGE UNCLASSIFIED | | | 19b. TELEPHONE NUMBER (Include area code) 391-394-0292 |

INTENTIONALLY LEFT BLANK.

Content

| | |
|---|-----------|
| 1. Introduction | 1 |
| 2. Reformer | 2 |
| 3. CO Removal Sub-System | 5 |
| 3.1 Water-Gas Shift Reaction..... | 5 |
| 3.2 Membrane Separator and Reactor | 6 |
| 3.3 Preferential Oxidation | 8 |
| 4. Putting Them Together | 10 |
| 5. Challenges for Using Diesel or JP-8 as Fuel | 12 |
| 5.1 Carbon Management | 13 |
| 5.2 Sulfur Management | 14 |
| 6. State-of-the-Art JP-8 and Diesel Reformers | 16 |
| 7. Conclusion | 17 |
| 8. References | 19 |
| Appendix A. Chemical and Physical Properties of Methanol, Diesel, and JP-8 | 25 |

List of Figures

| | |
|--|----|
| Figure 1. Permeation of hydrogen through a Pd-based membrane, in which (1) represents reversible dissociative chemisorption of hydrogen, (2) represents dissolution of atomic hydrogen, and (3) represents bulk diffusion of atomic hydrogen through the membrane..... | 7 |
| Figure 2. Conceptual block diagrams for fuel processing: A) A conventional fuel processing for diesel or JP-8, and B) Fuel processing for methanol..... | 11 |
| Figure 3. Carbon and sulfur balances for JP-8 or diesel fuel processing..... | 13 |
| Figure 4. Families of sulfur compounds in the JP-8 and diesel fuel..... | 16 |

List of Tables

| | |
|---|----|
| Table 1. Characteristics of various fuels for fuel reformation..... | 2 |
| Table 2. Partial oxidation offering compact size and steam reforming offering a high concentration of hydrogen | 3 |
| Table 3. Water-gas shift kinetic data over various metal-ceria catalysts..... | 6 |
| Table 4. Comparison of adiabatic and isothermal PROX reactors | 9 |
| Table 5. Key performance results of a 2% Pt/alumina sol-gel catalyst during PROX reaction with realistic post-water-gas shift reformat compositions [64]..... | 10 |
| Table 6. Selected qualities of low-sulfur crude [80]..... | 15 |
| Table 7. The reformer is robust to fluctuating sulfur content in the hydrocarbon feed stream [88]..... | 17 |
| Table 8. Testing of sulfur-tolerant catalysts for diesel and JP-8 steam reforming [74]..... | 17 |
| Table A-1. Selected chemical properties for methanol, JP-8, and diesel | 25 |

1. Introduction

Recently, Ball Aerospace has developed an advanced portable polymer electrolyte membrane (PEM) fuel cell system (4.2 by 7 by 7.8 inches, 6.5 lb) under the U.S. Army, Defense Advanced Research Project Agency (DARPA) and the Office of Special Technology (OST) [1]. With pure hydrogen fuel, this PEM fuel system can provide a normal 50-W power output for Army applications. Another PEM fuel cell power module (Nexa¹) is volume produced and is commercially available from Ballard. This state-of-the-art PEM fuel cell (22 by 10 by 13 inches, 29 lb) also converts high purity hydrogen fuel and oxygen to generate as much as 1200 W of unregulated electric power. One of the main drawbacks of using compressed hydrogen gas fuel is its low energy density compared with hydrocarbons. Another drawback is the source of hydrogen. An overview of several strategies of hydrogen generation and storage for PEM fuel cell has been reported previously [2]. Meanwhile, hydrogen is industrially produced by steam reforming of hydrocarbons such as methane, methanol, naphtha oil, etc [3–5]. The common goal for fuel processing research in many laboratories is to modify and miniaturize these industrial plants into fuel processors so that high purity hydrogen is produced on demand for fuel cells in portable, mobile, or stationary applications.

Unfortunately, a fuel reformer usually produces an appreciable amount of carbon monoxide (CO); therefore, a CO removal sub-system becomes an integral part of the fuel processor. At the operating temperature (<85 °C) of PEM fuel cell, CO adsorbs relatively strongly onto and thus poisons the fuel cell anode catalyst. Since the tolerable CO concentration is less than 10 parts per million (ppm), a fuel processor usually consists of both a reformer and a carbon monoxide removal sub-system.

At present, prototypes of complete fuel processor/fuel cell systems for portable, automobile, or residential applications have been developed, but none is ready to be commercialized. For example, Ballard and XCELLSiS have developed a methanol fuel processor that generates hydrogen on board the Mercedes-Benz (NECAR 5²). This fuel processor is compact enough to fit under the floor of the vehicle. In June 2002, DaimlerChrysler and Ballard announced that this fuel cell vehicle had completed an endurance drive from San Francisco, CA, to Washington, DC.

The main objective of this report is to discuss the challenges and the progress for the state-of-the-art fuel processor. This report focuses on hydrogen generation from reforming processes, and it is organized as follows. First, we demonstrate the general principles of fuel processing with state-of-the-art methanol fuel reformers as examples. Since the PEM fuel cell is the only kind of fuel cell that is being mass produced at this moment, research and development of carbon monoxide removal is important. Different approaches and recent efforts for carbon monoxide cleanup are included in this report. Finally, we address additional challenges and current status of logistic fuel (diesel and JP-8) reformers.

¹Nexa is a trademark of a PEM fuel cell module from Ballard.

²NECAR 5 is a fuel cell car from DaimlerChrysler.

2. Reformer

Considered as on-demand hydrogen generators for PEM fuel cells, fuel reformers have attracted lots of attentions. At this moment, details of methanol reforming [6–16] are better studied than other hydrocarbon fuels. There are reports on hydrogen generation from methane [17], ammonia [18], ethanol [19], kerosene [20] and diesel [21]. As the power need for soldiers becomes more demanding, diesel and JP-8 are good candidates as the main reforming fuels for Army applications because of logistics, transportability, flammability, and energy densities (see Table 1).

Table 1. Characteristics of various fuels for fuel reformation

| Fuel | Energy Density (kWh/kg, Lower Heating Value) | Logistics | Transportability | Flammability (Flash point in °F) |
|---|--|-----------|------------------|----------------------------------|
| H ₂ Storage (4-5wt%, compressed) | 0.7-0.9 [22] | No | Gas | Explosive |
| Methanol | 5.6 [23] | No | Liquid | 52 |
| JP-8 | 11.1 [24] | Yes | Liquid | 100 |
| Diesel | 11.8 [22] | Yes | Liquid | 160 - 210 |
| n-Octane | 12.3 [23] | No | Liquid | 56 |
| n-Dodecane | 12.3 [23] | No | Liquid | 160 |
| Propane | 12.8 [22] | No | Gas | -156 |

Although the infrastructure of the methanol supply is a problem, the potential of methanol fuel processing as an alternate supply of hydrogen is recognized for several reasons. First, methanol has a much higher specific energy than military primary and secondary batteries. Second, high conversion of methanol can be achieved at a relatively low temperature (250 to 300 °C). Finally, it is a bulk chemical produced in large quantities in chemical industry (12.5 billion gallons worldwide in year 2000).

Hydrogen generation from hydrocarbon or alcohol, e.g., methanol, can proceed by partial oxidation reforming (Equation 1) or by steam reforming (Equation 2).



In partial oxidation reforming, the air-to-fuel ratio for combustion is substoichiometric. This exothermic process can be performed in a catalytic manner or a non-catalytic manner. Catalytic partial oxidation is operated at lower temperature than non-catalytic partial oxidation. Catalytic partial oxidation also has a lower tendency for soot formation. Meanwhile, steam reforming is an endothermic process. The heat required for this process is provided by external sources. The advantages and disadvantages of partial oxidation reforming and steam reforming are shown in Table 2.

Table 2. Partial oxidation offering compact size and steam reforming offering a high concentration of hydrogen

| | Partial oxidation | Steam reforming |
|---------------|--|--|
| Advantages | Compact in size | High hydrogen concentration |
| | Fast start | |
| | Rapid transient response | |
| Disadvantages | Low H ₂ concentration in product gas, even when pure oxygen is used. Using air will further lower H ₂ concentration. | Strongly endothermic and typically limited by heat transfer (poor transient operation) |
| | Overall efficiency can suffer because of waste heat production. | Water supply and recycling required |
| | Catalyst deactivation because of excess heat. | Energy required to vaporize water with fuel |

Partial oxidation offers compactness, fast start, and rapid transient response, while steam reforming produces a higher concentration of hydrogen and thus higher system efficiencies. To improve the heat transfer properties for steam reformer, radial flow fuel processor [25], ceramic multiplayer fuel processor (1W_e) [26] and microchannel reactor [23] have been designed. In case of catalytic partial oxidation, steam is added into the reformer to control the temperature of the reforming process. This approach is very similar to autothermal reforming.

Autothermal reforming combines the heat effect of partial oxidation reforming and steam reforming so that autothermal reforming is operating under thermoneutrality ($\Delta H_r = 0$) [27]. Therefore, once the reactions are initiated during starting, no external heat is required. A small amount of precious metal catalyst (e.g., Pd/SiO₂) can provide the auto-ignition [28].

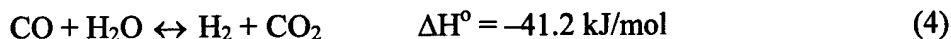
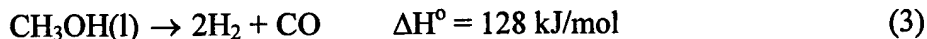
Thermodynamic calculations indicate that the autothermal reforming is the most efficient process [27,29]. In some cases, the autothermal reformer is usually configured into two compartments so that partial oxidation reaction occurs at the front and steam reforming occurs at the back [30]. Alternatively, the catalysts are designed so that steam reforming catalyst is close to the partial oxidation catalyst. For example, a layer of partial oxidation catalyst is deposited on the top of another layer of steam reforming catalyst on the monolithic substrate [31].

Meanwhile, several criteria apply to the catalysts. First, compact and lightweight reformers require very active catalysts. Second, high selectivity is important in order to simplify the carbon monoxide removal step. Moreover, the catalysts must be mechanically durable in order to withstand vibrations, especially for Army applications. Finally, long life span is advantageous to avoid frequent regeneration or recharging of catalysts.

Hydrogen generation by catalytic partial oxidation of methanol has been studied over Cu-Zn-based catalysts [12,14,15] and supported Pd catalysts [13]. A copper-based catalyst for this reaction is the most cost effective, but this kind of catalyst suffers from catalyst deactivation. Excessive heating causes copper particles to sinter, resulting in the loss of metal surface area [32].

Kinetic models and surface mechanisms for methanol steam reforming on Cu/ZnO/Al₂O₃ catalysts have been investigated [7,9,10,11,16]. Peppley, Amphlett, and others found that all

three reactions (steam reforming [Equation 2], methanol decomposition [Equation 3], and water-gas shift reaction [Equation 4]) must be included in the rate expression [10,11]. Although the methanol decomposition is much slower than the steam reforming, a small amount of CO can impede the performance of PEM fuel cell. Therefore, the methanol decomposition is included in the kinetic model.



In addition to kinetics for methanol steam reforming over a Cu/ZnO/Al₂O₃ catalyst, Agrell et al. have also explored the strategies for minimizing CO formation [7]. They found that increasing the steam-to-methanol ratio or adding oxygen/air effectively decreases CO formation. They also found that shortening the contact time and lowering the reactor temperature could suppress the reverse water-gas shift reaction.

Johnson Matthey has developed a modular methanol fuel processor (HotSpot³) [8]. In each module, both exothermic partial oxidation and endothermic steam reforming of methanol occur. By combining the appropriate number of individual reactors in parallel, the modular processor can be enlarged. A 245-cm³ processor can achieve steady state production 750 L of hydrogen per hour in 50 seconds from a cold start. Then the carbon monoxide level is reduced to < 10 ppm by a multistage catalytic microreactor (40% of the size of processor).

Battelle has recently developed a portable methanol steam reformer for the U.S. Army [23]. The reactor train includes a catalytic combustor, two vaporizers, and a microchannel steam reformer. Typically, fuel processor is operating at a temperature of 350 °C and a contact time of 140 ms. The estimated system energy density of the resulting fuel processor/fuel cell system is 720 Wh/kg for a 14-day mission.

Schuessler et al. have developed an autothermal methanol reformer with power density of 4 kW_e/kg or 10 kW_e/L [33]. The Cu/ZnO-based catalyst is deposited onto copper porous disks. Stacking these disks forms a monolithic radial flow reformer and enlarges the power requirement simultaneously. Since an isothermal temperature profile and a constant flow distribution are achieved, heat and mass transfers are not limiting with this reactor design. This design also offers a fast start. Within a minute, a temperature of 300 °C could be reached.

Membrane reactors [34,35] for methanol steam reforming have been tested. For example, Wieland, Melin and Lamm have developed membrane reactors using Pd₇₅Ag₂₅, Pd₆₀Cu₄₀ and Pd/V/Pd membranes [35]. The methanol and CO conversions in a membrane reactor are higher than equilibrium conversions in a conventional reactor because hydrogen is selectively removed in a membrane reactor. Membrane reactors are discussed in more details later.

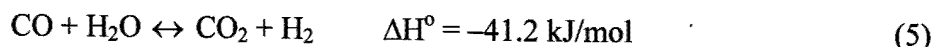
³ HotSpot is a trademark of a methanol fuel processor from Johnson Matthey.

3. CO Removal Sub-System

Since low temperature operation of the PEM fuel cell favors CO adsorption on anode catalysts, resulting in catalyst poisoning, a CO removal sub-system is an important component of a fuel processor. When the CO level in the hydrogen-rich reformat⁴ is on the order of 10%, the CO is usually removed by a water-gas shift reaction to a level of 1% or less. Then the CO level is further decreased to less than 10 ppm by preferential oxidation or by hydrogen-selective membrane separation.

3.1 Water-Gas Shift Reaction

The goal for a water-gas shift reactor is to reduce the CO level to less than 1% so that hot spots in the preferential oxidation unit can be avoided [36]. The water-gas shift reaction (Equation 5) is independent of pressure, and it is thermodynamically favored at low temperature.



Since the kinetics of the current catalyst are usually so slow at low temperature, a large catalyst volume is needed. The common practice is a two-stage shift reactor for high temperature shift reaction and low temperature shift reaction [4]. The high temperature shift step reduces the CO level to 2% to 3% at about 350 °C with iron and chromium oxide catalysts. Then the gas stream is cooled to about 200 °C for the low temperature shift reaction, which further reduces the CO concentration to about 1% or less. Cu/ZnO/Al₂O₃ is the most common commercial low temperature shift catalyst.

Although the water-gas shift reaction is well studied for reducing CO levels in a hydrogen stream in industrial applications, on-demand hydrogen generations in Army applications pose an entirely different set of challenges. In an industrial plant, the water-gas shift reactor continues to run most of the time. However, for on-demand hydrogen generation by a fuel processor, the water-gas shift catalysts go through lots of thermal cycles and on-off situations in which steam condenses. It is well known that water condensation deactivates the copper-based catalysts. The deactivation of Cu-based catalysts was discussed in detail recently [38].

Deactivation of commercial Cu/ZnO/Al₂O₃ water-gas shift catalysts is a major technical barrier. The state-of-the-art water-gas shift reactor consists of a long pre-reduction section to prevent metal agglomeration of copper-based catalyst. The volume of the shift reactors can occupy 50% of the volume of the entire fuel processor [37]. The state-of-the-art water-gas shift reactor for a 50-kW fuel processor is about 20 to 40 kg and 20 to 40 L [39]. Unless the size of water-gas shift reactor is reduced through the development of a better catalyst, it is impractical to use fuel-processing technology to provide power for Army applications. In addition, the pyrophoric nature of these high and low temperature catalysts in their active states is a safety issue for the users [37]. Replacing catalysts or any accidental exposure to air at an unsafe temperature will endanger soldiers' lives.

⁴ Reformat⁴ refers to the product stream from a reformer.

In literature, there are some recent attempts to develop better water-gas shift catalysts, and metal-based cerium oxide catalysts are promising candidates [40–44]. Activation energy, E_a , for some kinetic studies are summarized in Table 3.

Table 3. Water-gas shift kinetic data over various metal-ceria catalysts

| Metal Loading | Support | E_a , kJ/mol | Reference |
|---------------|----------------------|----------------|-----------|
| None | Ceria | 63 \pm 4 | [40] |
| Pt | Ceria | 46 \pm 4 | [40] |
| Rh | Ceria | 46 \pm 4 | [40] |
| 1% Pd | Ceria | 38 | [41] |
| 1% Ni | Ceria | 44 | [41] |
| None | Ce(La)O _x | 58.5 | [42] |
| 5% Ni | Ce(La)O _x | 38.2 | [42] |
| 5% Cu | Ce(La)O _x | 30.4 | [42] |

The enhancement of water-gas shift activity by base metals has been attributed to a synergistic redox reaction. The metal components increase the oxygen storage capacity and reducibility of pure ceria [40,42].

Recently, there have been many studies of the catalysis by nanosized gold particles, including water-gas shift reaction [45]. Andreeva et al. [46] have studied the catalytic activity of Au/ZnO, Au/ZrO₂, Au/Fe₂O₃, Au/Fe₂O₃-ZnO, and Au/Fe₂O₃-ZrO₂ catalysts for water-gas shift reaction between 140 and 360 °C. The catalysts are prepared by deposition-precipitation method. The results have shown that the water-gas shift activity strongly depends on the dispersion of gold particles, as well as the state and the structure of the supports. In another study, water-gas shift activities of gold, silver, and copper particles nano-dispersed on TiO₂ have been compared [47]. The order of activities has determined to be gold > copper > silver (no activity). The Fourier transform infrared (FTIR) data indicate that the differences in activities are attributable to the ability to adsorb CO. In addition, a high water-gas shift activity by Au/CeO₂ with loading of 1% to 8% has been demonstrated at low temperature [43,44]. The transmission electron microscopy (TEM) results indicate that the nanosized gold particles are stable and preserved after the reaction [44]. The temperature-programmed reduction (with 20% H₂/N₂) results show that the addition of gold drastically increases the oxygen reducibility of ceria [43].

Since many of the recent water-gas shift research efforts are driven by the need for a better three-way catalyst (TWC), irreversible reducibility of the catalyst was not an issue. However, hydrogen concentration is as high as 75% for fuel processing applications. It is important to have a water-gas shift catalyst that can function properly at this high hydrogen concentration regime. Recently, Zalc, and others [36] have tested the activity and the stability of several Pt-based ceria catalysts with typical reformat compositions. Low activity and rapid first order deactivation are observed. These results suggest that a high hydrogen concentration in reformat leads to irreversible over-reduction of the ceria in these Pt-based catalysts.

3.2 Membrane Separator and Reactor

Membrane reactors couple chemical reaction with membrane separation. They have received growing attention for fuel processing in recent years. A monograph [48], reviews [49–51] and conferences such as the International Conference on Catalysis in Membrane Reactors (ICCMR)

have been dedicated to this subject. The most attractive feature is that membranes can potentially surpass the equilibrium conversion by removing one of the reaction products, usually hydrogen, selectively.

Among several types of membrane, the Pd-based membrane has the highest selectivity for hydrogen. The membrane separation process is based on the selective diffusion of hydrogen through a high temperature metal membrane. An elevated pressure is required on the “feed” side. The hydrogen permeation rate is directly proportional to the difference in the square roots of hydrogen pressures between the feed and permeation sides of the membrane. One of the major challenges is the trade-off between mass transfer resistance and structural integrity. A thin membrane has a lower mass transfer resistance and therefore requires lower pressure difference between the high pressure side and low pressure side of the membrane. However, the membrane will become brittle during thermal cycling as the thickness decreases. Therefore, durability has been one of the main issues. Also, the fact that the high hydrogen is usually generated at the low pressure from the reformer reduces the advantage of using this process. Usually, a compressor or a sweep gas is needed.

The permeation of hydrogen through the Pd membrane is a multi-step process [49]:

1. reversible dissociative chemisorption of hydrogen on the membrane surface;
2. reversible dissolution of surface atomic hydrogen in the bulk layers of Pd; and
3. diffusion of atomic hydrogen in the membrane.

Figure 1 illustrates this multi-step process.

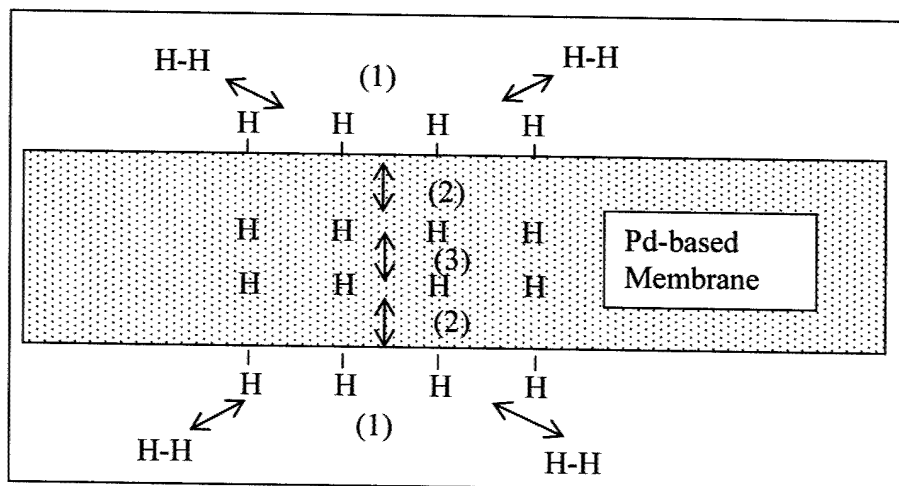


Figure 1. Permeation of hydrogen through a Pd-based membrane, in which (1) represents reversible dissociative chemisorption of hydrogen, (2) represents dissolution of atomic hydrogen, and (3) represents bulk diffusion of atomic hydrogen through the membrane.

With regard to fuel-processing applications, the membranes need to have high hydrogen permeability and selectivity, combined with good chemical, mechanical and thermal long-term stability [52]. For example, a few cycles of $\alpha \leftrightarrow \beta$ phase transition of pure Pd result in severe

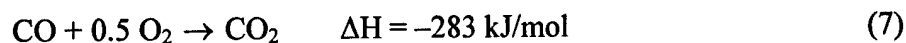
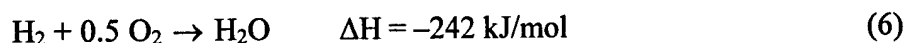
lattice strains. Therefore, Pd alloy membranes such as Pd-Ag have been studied extensively as a membrane candidate to reduce the strains. Other current limitations for commercial use of Pd membranes have been discussed elsewhere [52]. Composite membranes are believed to be the most reasonable choice for producing high purity hydrogen [53,54]. These membranes consist of 1) a thin metallic layer that is only permeable to hydrogen, and 2) a porous substrate that provides mechanical support to the thin metal. In some cases, the porous material also prevents the direct contact of the metal layer and the water-gas shift catalyst [55].

The effect of the feed composition on the membrane reactor efficiency has been studied by Criscuoli et al. [55]. Their cylindrical reactor is 28 cm long with a 15-cm-long inner tube (70- to 75- μ m thick palladium membrane) and stainless steel outer tubes (4 cm inner diameter). The water-gas shift catalyst from Topsøe was packed in the inner tube with porous alumina separating the membrane and the catalyst. Criscuoli et al. have tested mixtures of different compositions with traditional fixed bed, mesoporous ceramic membrane and palladium membrane reactors. With the palladium membrane, it is possible to reach higher conversions than the equilibrium values. For example, the CO conversion for reformat composition (12% CO, 12% CO₂, 75% H₂, and 1% CH₄) at 595 K is about 51% (about 2% higher than equilibrium value).

However, the applications of membrane reactor in fuel reforming are limited by the quality of the reactant stream available [56]. The influences of CO [35,57], sulfur [58,59] and steam [57] on permeability have been studied. Note that CO, H₂S, and steam are usually present in the reformat from diesel or JP-8 reformer. The effect of CO on permeability is flow rate dependent. The presence of steam has a pronounced effect on the hydrogen permeability [57].

3.3 Preferential Oxidation

A typical gas stream following the water-gas shift reaction still contains about 1.0% CO, which is still too high for the low temperature PEM fuel cell. Therefore, preferential oxidation (PROX) is performed to reduce the CO in the feed to 10 ppm or less. However, hydrogen oxidation competes with CO oxidation:



Since the enthalpies of these reactions are highly exothermic, heat removal from the reactor is important. In order to reduce CO concentration and to minimize the undesirable hydrogen oxidation, highly selective (preferential oxidation) catalysts are necessary. Since CO adsorbs more strongly to the Pt surface than hydrogen does, this fact can be used for selective oxidation. Low Pt loading on γ -alumina is commonly used because of its low tendency for hot spots [32].

Preferential oxidation reactors may be either adiabatic or isothermal [60]. The characteristics of these reactors are compared in Table 4.

Table 4. Comparison of adiabatic and isothermal PROX reactors

| | Adiabatic | Isothermal |
|---|---|--|
| Temperature of Catalyst | Allowed to rise during CO oxidation. | Maintained constant during CO oxidation. |
| Number of Stages | A number of sequential stages progressively reduce the CO content. | One or two stages. |
| Concern of Reverse Water-Gas Shift (RWGS) | Temperature control is important to prevent RWGS which forms more CO. | No concern on this issue. |

Noble metal-based catalysts are the most common PROX catalysts. For example, Engelhard has started commercializing a highly selective Pt containing catalyst (Selectroxo⁵) for H₂ production plants in 1960s. During steady state conditions (50 °C, 10,000 h⁻¹ and 200 to 400 psig), the present catalyst reduces the CO level from 1% to less than 5 ppm [61]. Although the PROX catalyst is well developed in industrial scale, a new catalyst needs to be developed for fuel cell applications. Ambient pressure, low temperature, and small residence time (i.e., fast space velocity) are preferred in fuel cell applications. Smaller residence time corresponds to more compact PROX reactor.

Engelhard has recently developed an iron oxide promoted Pt(5%)/ γ -alumina catalyst for preferential oxidation of CO [61,62]. The promoted Pt catalyst on the monolith reduces the CO level (1000 ppm inlet CO) with 90% conversion and 65% selectivity at 90 °C and 120,000h⁻¹. The results also indicate that iron oxide changes the electronic properties of Pt metal particles. The iron oxide also creates a dual site non-competitive mechanism for CO oxidation [62].

In a previous study, Watanabe et al. have shown that 6% Pt-supported zeolite can oxidize CO much more selectively in 78% to 98% hydrogen than can a conventional Pt-supported alumina catalyst [63]. With 0.5% O₂ and 1% CO, the selectivity is affected by type of zeolite supports, in the order A type zeolite (88%) > mordenite (84%) > X type zeolite (64%) > alumina (41%). Watanabe et al. have designed a two-stage Pt-mordenite PROX reactor that uses 0.7% oxygen to remove 1% CO with a loss of 0.4% H₂.

In contrast to aforementioned studies [61,62,63], Gulari et al. [64], and General Motors [60] have tested the PROX catalysts using a realistic reformat composition with the presence of both CO₂ and H₂O. Gulari et al. argue that a realistic composition of reformat from water-gas shift reactor contains CO₂, CO, H₂, and H₂O, and all these species tie together by the (reverse) water-gas shift reaction [64]. Gulari et al. have shown that a 2% Pt/alumina sol-gel catalyst can selectively oxidize CO to less than 5 ppm. Gulari et al. results also indicate that CO₂ in the feed retards the CO oxidation, but water in the reformat promotes the CO oxidation. More importantly, Gulari et al. have shown that the combination of 20% CO₂ and 10% water in the reformat increases the

⁵ Selectroxo is a trademark of a PROX catalyst from Engelhard.

CO conversion. Some of their results are summarized in Table 5. Based on the results in Table 5, Gulari et al. have proposed an optimal design for a PROX reactor that removes more than 0.5% CO. Their proposed design has several stages with an injection port for air or oxygen at each stage.

Table 5. Key performance results of a 2% Pt/alumina sol-gel catalyst during PROX reaction with realistic post-water-gas shift reformat compositions [64]

| | Case I | Case II |
|-----------------------------|--|--|
| Feed Composition | 1% CO, 20% CO ₂ , 60% H ₂ , 10% H ₂ O and He as balance | 0.5% CO, 20% CO ₂ , 60% H ₂ , 10% H ₂ O and He as balance |
| O ₂ -to-CO ratio | 1 | 1 |
| Optimal Temperature | 160 °C | 140 to 150 °C |
| Conversion | 99% | 100% (sensitivity of 5 ppm) |
| Selectivity | 48% | 50% |

Investigators at General Motors have developed an iridium-based catalyst to oxidize CO selectively in hydrogen-rich feed gas [60]. About 2% iridium is dispersed on a refractory oxide washcoat such as alumina. Then a mixture of methanol and hydrogen activates the catalyst. An activation method is developed to lower the binding energy and oxidation state of the iridium. At a temperature of about 230 °C and O₂-to-CO of 2 (excess O₂), 0.55% CO was decreased to 10 ppm. The residence time is on the order of 50 milliseconds, which is much smaller than 360 milliseconds (corresponds to 10,000 h⁻¹) in industrial scale.

4. Putting Them Together

The integration of reforming reaction and water-gas shift reaction in a methanol reformer eliminates the need for a separate water-gas reactor. This simplifies the process flow sheet and potentially improves the dynamic response of the system (see Figure 2).

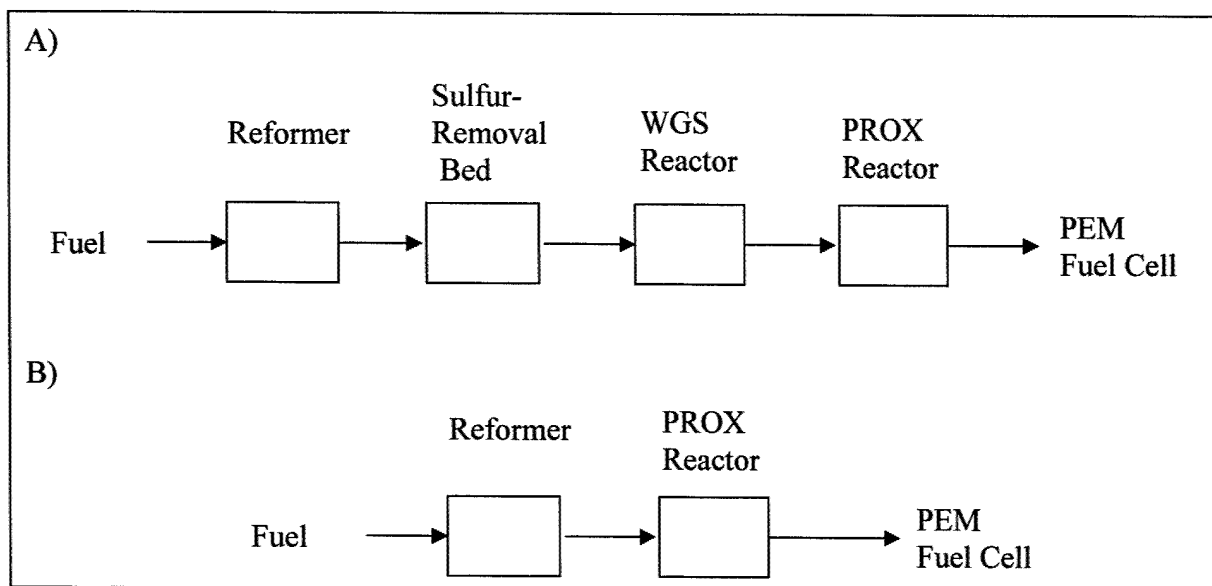


Figure 2. Conceptual block diagrams for fuel processing: A) A conventional fuel processing for diesel or JP-8, and B) Fuel processing for methanol.

Development of the integration of a fuel cell and fuel processor into a complete functional unit is very active [26,29,65]. As aforementioned, DaimlerChrysler, Ballard, and XCELLSiS have jointly developed the NECAR 5 by using a compact size methanol reformer underneath the seats. This 75-kW fuel processor (ME 75-5) consists of three integrated components [65]: 1) vaporizer and superheater in a combined catalytic burner/vaporizer, 2) a combined reformer and preferential oxidation reactor, and 3) a novel reactor allowing exothermic, autothermal, and endothermic operations. All these components operate around 250 to 300 °C.

One of the major technical challenges is the dynamic or transient response of the system. When there is a load change in power usage, the fuel processor has to respond appropriately to maintain a low level of CO. In other words, CO spikes should be prevented. For instance, the fuel flow rate will be slow until the power usage decreases. The gas compositions of the reformatte feeding into the PEM fuel cell will change dramatically unless (1) the system is properly controlled, (2) the reactor is designed appropriately as well as (3) the catalyst composition in each unit is optimized for different feed compositions. At a very low output (<10% of maximum), the use of a low fuel feed rate to the reactor can result in methanol slip and above average CO concentration [8]. Vandeborgh, Springer, and Huff at Los Alamos National Laboratory, NM, have described a recycle steam reforming reactor to achieve quick start and to address the transient operation [66].

The modular feature of Johnson Matthey HotSpot fuel processor described earlier can provide an extra control option during transient operation [8]. The hydrogen output can be increased or decreased by the use of more or fewer active reactors, instead of increasing or decreasing the reactant feed rates.

Ford researchers have proposed using metal hydride bed as a load-leveling device and gaseous hydrogen supply for start [67,68]. One of the designs includes a single metal hydride bed and

two hydrogen purification units in series [67]. The metal hydride bed stores hydrogen at high hydrogen concentration while the bed discharges hydrogen at low hydrogen concentration. Each hydrogen purification unit consists of a highly selective membrane that preferentially passes hydrogen molecules. The first hydrogen purification unit receives a supply of high pressure reformat, and the permeated portion supplies hydrogen to the metal hydride bed. The non-permeated portion enters the second hydrogen purification unit. The fuel cell receives hydrogen from both the second purification unit and the metal hydride bed in a parallel fashion.

In another study, a fuel cell drive system was constructed by the integration of a 16-kW catalytic burner, a 50-kW methanol reformer, and a PEM fuel cell [67]. The performance and dynamic behavior were tested. Stationary performance shows hydrogen production of $6.7 \text{ m}^3/(\text{kg}_{\text{cat}} \text{ h})$ with 95% methanol conversion at 280°C . Several peak load storage systems were also compared. A gas storage system was selected and integrated in the system. The transient behavior was measured, and the response time for reaching 99% hydrogen demand was about 20 s.

Since methanol is usually not steam reformed completely, unreacted methanol is undesirably fed to the anode side of PEM fuel cell operating at low temperature. For this reason, the starting voltage is greatly reduced. Okamoto at Honda [70] has suggested that either the unreacted methanol is selectively oxidized via a noble catalyst, or the unreacted methanol is oxidized together with carbon monoxide. He also proposed that the unreacted methanol can be condensed and then be returned to the methanol tank.

Thermal management is another challenge in system integration. General Motors has thermally integrated a two-stage methanol reformer [71]. The stream from the first stage reformer acts as the heat transfer medium, which carries heat from the heat exchanger into the reactors. The heat exchanger and two reactors are co-located in a common housing. In another study, Daimler-Benz (now DaimlerChrysler) assembled a three-stage fuel processor with thermal coupling [72]. $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ pellets are packed inside all three stages of the steam reformer. The center stage is heated externally to 280 to 350°C but the inlet stage and the outlet stage are not. The inlet stage and the outlet stage are divided by a highly heat-conducting but gas-tight wall. This design has three main advantages for transient response during load changes. First, temperature fluctuations in center reactor stage are dampened because of heating capacity of the outlet-side stage. Second, the fluctuations of CO content in the reformat are also reduced. Third, a self-regulating heat transfer is implemented because of thermal coupling of the inlet side with the outlet side.

5. Challenges for Using Diesel or JP-8 as Fuel

Unlike methanol, diesel and jet fuels consist of numerous components. These fuels, which are obtained by petroleum refinery of crude oil, have many grades with different properties. Selected chemical and physical properties of methanol, JP-8, and diesel are summarized in Appendix A.

Diesel or JP-8 reforming requires a higher temperature (usually about 1000°C) than methanol reforming (200 to 300°C). Higher temperature favors hydrogen production, but it also enhances catalyst deactivation (through thermal sintering of catalyst) and formation of carbonaceous species. Higher temperature also requires better thermal management strategies such as a

sophisticated integration of heat exchanger network and/or novel insulation materials so that the fuel processor can be built compact enough for portable and mobile applications. This report focuses on two main challenges using logistic fuel reformers to generate hydrogen for PEM fuel cells: 1) carbon management, and 2) development of sulfur-tolerant catalysts. Figure 3 shows the conversion pathways of carbon- and sulfur-containing compounds during fuel processing. We emphasize that all these carbon-containing species from the reformer originate from the reaction and are not generally impurities. Meanwhile, the sulfur species come from the impurities, such as benzothiophenes (BT) and dibenzothiophenes (DBT), in the refinery products after hydrodesulfurization (HDS).

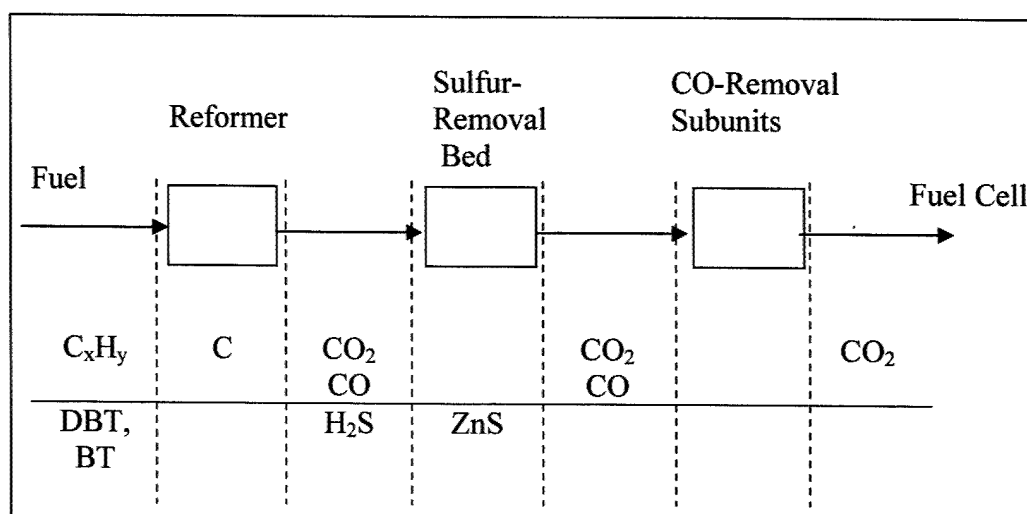


Figure 3. Carbon and sulfur balances for JP-8 or diesel fuel processing.

5.1 Carbon Management

Carbon management involves minimization of carbonaceous species accumulation, as well as optimization and removal of carbon-containing gaseous species. After reforming, the hydrocarbons in diesel fuel or JP-8 can become CO , CO_2 , CH_4 , coke, and soot.

The CO , CO_2 , and CH_4 management is similar to methanol reforming, which has been discussed earlier. The main difference is the level of CO concentration. Brown at Los Alamos National Laboratory has compared methanol, JP-8, and diesel for the utility as hydrogen source [73]. Thermodynamic calculations indicate that high temperature produces a large amount of CO . The equilibrium CO level from diesel or JP-8 reformer can be as high as 25%, which is much higher than 0.8% CO from methanol reformer [73]. Experimental results show that diesel steam reforming gives 16% CO in the reformat [74]. Therefore, separate water-gas shift reactors are required. The issue here is about the fuel-reforming thermodynamics that control the proportion of these gases. The level of CO needs to be minimized without forming too much CH_4 so that the CO removal process is simplified. Recall that the CO tolerance level for anode catalyst in low temperature PEM fuel cell is about 10 ppm. The common strategy is to optimize the operating conditions such as space velocity, steam-to-C ratio and air-to-C ratio.

Carbon formation, including formations of coke and soot, can arise from the thermal cracking of hydrocarbons (pyrolysis) or can be promoted by a catalyst [75]. Coke that deposits on the catalyst will deactivate the catalyst. Carbon deposition on the wall of the reactor affects the reactor performance by limiting heat transfer and ultimately blocking the flow. During start, autothermal reformers produce soot particles. Soot (smoke) prevention is an important practical issue for Army applications. Soldiers do not like to lose their camouflage because of smoke.

When diesel contacts a hot surface in the reformer, it has tendency to form coke. Non-ideal mixing of fuel with the air and the steam also enhances coke formation, and fuel injection through an atomizer is often used to avoid this problem. The formation of solid carbon has been investigated from a thermodynamic point of view [29]. Formations of coke and soot depend on the ratio of carbon and hydrogen in the fuel, air-to-carbon ratio, steam-to-carbon ratio. Docter and Lamm at Daimler-Benz performed thermodynamic calculations to find the optimal operating conditions for gasoline reformers. Their results indicate that a high steam-to-carbon ratio shifts the coking boundary to a lower air-to-carbon ratio.

Trimm [75] has also reviewed various approaches to minimize coke accumulation. The coke accumulation is a balance between coke formation and coke gasification. The first approach is the ensemble size control. It is believed that the ensemble size of surface sites for coke formation is larger than that for steam reforming. Therefore, controlling the ensemble size can minimize polymerization of monatomic carbon species. This can be done by adsorption of a trace amount (ppm level) of sulfur. For example, an H_2S -to- H_2 ratio that is greater than 7.5×10^{-7} was sufficient to control the coke formation. The second approach is to prevent the carbide formation by the addition of small amount of dopants. For example, 0.5% tin to nickel reduces coke formation significantly while steam reforming is not affected. The third approach is to accelerate the coke gasification. On a nickel steam-reforming catalyst, coke forms when carbon fibers (whiskers) grow with a nickel crystal at the top. When noble metals are used, the whisker growth mechanism is blocked simply because carbon is not dissolved [76]. Excess steam is usually fed into the steam reformer to enhance gasification. In industries, Topsøe uses magnesia as catalyst support materials because magnesia enhances the adsorption of steam. Adding rare earth oxides such as ceria to the support materials also appears to favor coke gasification.

5.2 Sulfur Management

Unlike methanol, diesel and JP-8 are mixtures of many organic compounds including sulfur-containing compounds. Sulfur in fuel poisons and deactivates the reforming catalysts [77]. Typically, catalytic steam reforming of hydrocarbon is achieved by a nickel catalyst. But nickel catalysts are very sensitive to sulfur-containing compounds. Therefore, the fuel is usually pre-reformed to reduce sulfur to less than 1 ppm. An alternative is to allow the nickel catalyst to be poisoned, but the reformer operates at a higher temperature and with a larger volume of catalysts. Another choice is to use more expensive noble metal such as platinum, palladium, or rhodium instead of nickel. These noble metal catalysts are better than nickel, but sulfur poisoning is still an issue.

During reforming, these sulfur compounds are converted to mainly H₂S and possibly COS, which are commonly removed by a ZnO scrubber.



Equation (8) explains why Cu/ZnO/Al₂O₃ methanol reforming catalyst cannot be a good catalyst for diesel or JP-8 reforming. However, the reducibility or regenerative ability of ZnO above 400 °C has been a major issue for this adsorbent. Therefore, Cu-containing cerium oxide has been examined as an alternative [78].

It is noteworthy that H₂S is an irreversible poison for Pd membrane separator and fuel cell. The use of membranes in enhancing H₂ production from diesel or JP-8 is limited by the quality of the reactant stream. Several recent reviews indicate that the reactants containing CO and H₂S or aromatics are “unacceptable” because of their tendency to poison Pd surfaces [79]. In a previous study [58], the effect of carbon or sulfur on the permeation rate of hydrogen through a palladium membrane was investigated. These impurity atoms block the surface adsorption site of hydrogen. It has been determined that the permeation rates of hydrogen vary by a factor of ~10⁴ as sulfur or carbon coverage increases from 0.06 to 0.65 at 625 K.

In another study [20], the Ru/CeO₂-Al₂O₃ catalyst shows high sulfur resistance during steam reforming of kerosene (C₁₀H₂₂). JP-8 is a kerosene-type aviation turbine fuel. The addition of CeO₂ to Ru/Al₂O₃ increases the sulfur tolerance from 0.1 to 50 wt ppm of sulfur. Both Ru/Al₂O₃ and Ru/CeO₂-Al₂O₃ start with 100% conversion of kerosene (with 50 wt ppm sulfur) at 800 °C and steam/carbon = 3.5. After 25 hours, the conversion using Ru/Al₂O₃ decreases to 60% while the conversion using Ru/CeO₂-Al₂O₃ was 66%.

The sulfur content and sulfur-containing components of crude oil depend on the geographic location of the oil field. Some crude oils are more “sour” than others. As a result, sulfur contents in fuel products are also different [80].

Table 6. Selected qualities of low-sulfur crude [80]

| Crude Oil (Region) | Crude Sulfur (wt%) | Sulfur in middle distillates, 175 to 350 °C (wt%) |
|----------------------------|--------------------|---|
| Arab Light (Middle East) | 1.9 | 0.9 |
| Bonny Medium (West Africa) | 0.2 | 0.1 |
| Brega (North Africa) | 0.2 | 0.1 |
| Minas (Far East) | 0.1 | 0.0 |

Government regulations often dictate sulfur content in diesel products [81,82]. In the European Union, the sulfur content is limited to 350 wt ppm today and will be lowered to 50 wt ppm by 2005 [77,81]. In America, the current sulfur content limit is 500 wt ppm [83], and the Environmental Protection Agency target by mid 2006 is 15 wt ppm. The specifications for sulfur content in jet fuels are given by military specifications MIL-DTL-5624 and MIL-DTL-83133E.

Hydrodesulfurization (HDS) reduces the sulfur content in the crude oil to the acceptable level in diesel products. The remaining sulfur compounds are usually alkylbenzothiophenes (alkyl BT) and alkyldibenzothiophenes (alkyl DBT) (see Figure 4) because they are the most difficult sulfur compounds to be removed [84,85].

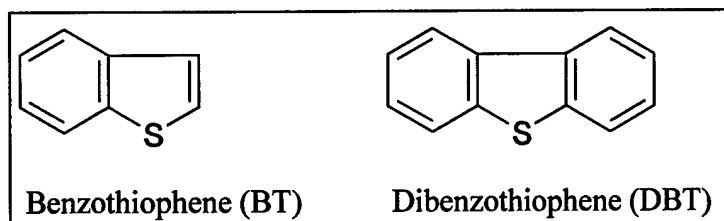


Figure 4. Families of sulfur compounds in the JP-8 and diesel fuel.

For example, sulfur-containing compounds in D-2 diesel from America are present as 33 to 35 wt% BT and 65 to 67 wt% DBT [86]. The weight percent of sulfur-containing compounds and the proportion of BT and DBT in diesel products depend on the origin of the crude and the refinery processes. If the Army fuel processor is robust enough to tolerate the sulfur-containing compounds in diesel fuels from global wartime suppliers, the logistic burden for fuel supply during wars will be improved.

6. State-of-the-Art JP-8 and Diesel Reformers

Jet fuel reformation for fuel cell system has been the subject of investigation as early as 1960's [87]. The steam reformer with 25 cm³ of catalyst was tested on stream for 28 hours. A high steam-to-hydrocarbon ratio (>5) was used to avoid coking. At 972 °F (522 °C), JP-4 with 80 ppm of sulfur was steam reformed to 65% hydrogen in product gas. However, there is no information regarding the nature of the catalyst.

In a recent patent assigned to Allied Signal, a catalytic partial oxidation reformer was developed for JP-8 [88]. With the method of incipient wetness, 5 to 30 wt% rhodium is supported on the 100 mg of alumina monolith support. The finished catalyst was held in a 0.5-inch quartz tube and was tested for partial oxidation reforming of heavy hydrocarbons. Some of the operating conditions and results are summarized in Table 7.

In another patent, steam reforming reformer was developed for diesel and JP-8 [74]. The catalyst extrudates (1/16 inch outer diameter, 4 cm long) consist of three components:

- active catalyst phase such as Ag, Co, Cu, Fe, Pd, Pt, V
- promoter such as Bi₂O₃, CaO, La₂O₃, MgO, Pr₆O₁₁, and
- support such as CeO₂, Mullite, ZrO₂.

Table 7. The reformer is robust to fluctuating sulfur content in the hydrocarbon feed stream [88]

| Hydrocarbon feed | JP-8 without alternation | JP-8 with addition of 1000 ppm dibenzothiophene |
|-------------------------------------|--------------------------|---|
| Loading of Rh (wt%) | 21 | 25 |
| C/O ratio | 0.8 | 0.8 |
| Catalytic Temperature (°C) | 1150 | 1220 |
| Contact Time (ms) | 100 | 100 |
| Hydrogen gas yield(%) | 80-85 | 70 |
| Carbon monoxide gas yield (%) | 90-93 | 70-80 |
| Run time for stable Operation (hrs) | 500 | 300 |

The packed bed reactor with these extrudates has been tested with JP-8 jet fuel and DF-2 diesel fuel. There is a temperature gradient along the catalyst bed. During the operating conditions shown in Table 8, the catalyst is sulfur tolerant and exhibits stable performance until 500 hours (for JP-8) without coking. Complete conversions of both fuels are observed. The composition of the product gas (dry basis) from the diesel steam reformer is 63% H₂, 20% CO₂, 16% CO, and 1% CH₄. The residence time of 1 to 2 seconds implies that the reformer size is quite large.

Table 8. Testing of sulfur-tolerant catalysts for diesel and JP-8 steam reforming [74]

| Hydrocarbon feed | DF-2 | JP-8 |
|---------------------------------|------|------|
| Fuel flow rate (ml/hr) | 6.1 | 6.8 |
| H ₂ O/C ratio | 3.8 | 4.7 |
| Residence Time (ms) | 1654 | 1182 |
| Inlet catalyst temperature (°C) | 370 | 360 |
| Outlet catalyst temperature(°C) | 1000 | 1000 |
| Run time (hrs) | 276 | 504 |

7. Conclusion

Fuel reformer can generate hydrogen from methanol, JP-8, and diesel. Since the PEM fuel cell anode catalyst has low CO tolerance (10 ppm), the reformat from the fuel reformer is fed into CO removal units before PEM fuel cell. At this moment, the development of a methanol fuel processor is more advanced than that of JP-8 or diesel. This report has provided examples that show that methanol fuel processor can be combined with PEM fuel cell to generate power (1 W to 75 kW) for Army applications. Although the reforming catalysts and the operation parameters will be different for different feedstock, the concepts and the general principles of processing different fuels are very similar in many aspects. The principles of fuel reforming, the applications of thermodynamics as guidance, the options for carbon monoxide removal, the ideas of reactor design and enlargement, as well as the system integration strategies for start and transient response are usually fuel independent. Therefore, the experience gained during the development of methanol fuel processors is very helpful for the development of diesel and JP-8 fuel processors. However, the chemical nature of JP-8 or diesel is significantly different from that of

methanol. This difference poses additional challenges. Carbon and sulfur managements have to be addressed to advance the technology of JP-8 and diesel fuel processors for Army applications. In addition, better CO removal strategy is necessary because logistic fuel reformers produce reformat gases containing high CO concentration.

8. References

1. Chu, D., Jiang, R., Gardner, K., Jacobs, R., Schmidt, J., Quakenbush, T. and Stephens, J., "Polymer Electrolyte Membrane Fuel Cells for Communication Applications," *J. Power Sources* 96 (2001) 174.
2. Walker, C. W. Jr., Jiang, R. and Chu, D., "An Overview of Hydrogen Generation and Storage for Low-Temperature PEM Fuel Cells," *ARL-TR-2091*, Army Research Laboratory (1999).
3. Farrauto, R. J. and Bartholomew, C. H., *Fundamentals of Industrial Catalytic Processes*, Blackie Academic and Professional, London (1997).
4. Twigg, M. V. (Ed.) *Catalyst Handbook*, 2nd Edition, Wolf Publishing, London (1989).
5. Gates, B. C., Katzer, J. R. and Schuit, G. C. A., *Chemistry of Catalytic Processes*, McGraw-Hill, New York (1979).
6. Geissler, K., Newson, E., Vogel, F., Truong, T., Hottinger, P. and Wokaun, A., "Autothermal Methanol Reforming for Hydrogen Production in Fuel Cell Applications," *Phys. Chem. Chem. Phys.* 3 (2001) 289.
7. Agrell, J., Birgersson, H. and Boutonnet, M., "Steam Reforming of Methanol over a Cu/ZnO/Al₂O₃ Catalyst: A Kinetic Analysis and Strategies for Suppression of CO Formation," *J. Power Sources* 106 (2002) 249.
8. Edwards, N., Ellis, S. R., Frost, J. C., Golunski, S. E., van Keulen, A. N. J., Lindewald, N. G. and Reinkingh, J. G., "On-Board Hydrogen Generation for Transport Applications: the HotSpotTM Methanol Processor," *J. Power Sources* 71 (1998) 123.
9. Lindström, B. and Pettersson, L., "Hydrogen Generation by Steam Reforming of Methanol over Copper-Based Catalysts for Fuel Cell Applications," *Int. J. Hydrogen Energy* 26 (2001) 923.
10. Peppley, B. A., Amphlett, J. C., Kearns, L. M. and Mann, R. F., "Methanol-Steam Reforming on Cu/ZnO/Al₂O₃ Catalysts. Part 1: The Reaction Network," *Applied Catalysis A: General* 179 (1999) 21.
11. Peppley, B. A., Amphlett, J. C., Kearns, L. M. and Mann, R. F., "Methanol-Steam Reforming on Cu/ZnO/Al₂O₃ Catalysts. Part 2. A Comprehensive Kinetic Model," *Applied Catalysis A: General* 179 (1999) 31.
12. Alejo, L., Lago, R., Pena, M. A. and Fierro, J. L. G., "Partial Oxidation of Methanol to Produce Hydrogen over Cu-Zn-Based Catalysts," *Applied Catalysis A: General* 162 (1997) 281.
13. Cubeiro, M. L. and Fierro, J. L. G., "Partial oxidation of Methanol over Supported Palladium Catalyst," *Applied Catalysis A: General* 168 (1998) 307.

14. Velu, S., Suzuki, K. and Osaki, T., "Selective Production of Hydrogen by Partial Oxidation of Methanol over Catalysts Derived from CuZnAl-Layered Double Hydroxides," *Catalysis Letters* 62 (1999) 159.
15. Agrell, J., Hasselbo, K., Jansson, K., Jaras, S. G. and Boutonnet, M., "Production of Hydrogen by Partial Oxidation of Methanol over Cu/ZnO Catalysts Prepared by Microemulsion Technique," *Applied Catalysis A: General* 211 (2001) 239.
16. Asprey, S. P., Wojciechowski, B. W. and Peppley, B. A., "Kinetic Studies using Temperature-Scanning: The Steam-Reforming of Methanol," *Applied Catalysis A: General* 179 (1999) 51.
17. Krumpelt, M., Kumar, R. And Myles, K. M., "Fundamentals of Fuel Cell System Integration," *J. Power Sources* 49 (1994) 37.
18. Choudhary, T. V., Sivadinarayana, C. and Goodman, D. W., "Catalytic Ammonia Decomposition: CO_x-Free Hydrogen Production for Fuel Cell Applications," *Catalysis Letters* 72 (2001) 197.
19. Rampe, T., Heinzl, A. And Vogel, B., "Hydrogen Generation from Biogenic and Fossil Fuels by Autothermal Reforming," *J. Power Sources* 86 (2000) 536.
20. Suzuki, T., Iwanami, H. and Yoshinari, T., "Steam Reforming of Kerosene on Ru/Al₂O₃ Catalyst to Yield Hydrogen," *International Journal of Hydrogen Energy* 25 (2000) 119.
21. Amhlett, J. C., Mann, R. F., Peppley, B. A., Roberge, P. R., Rodrigues, A. And Salvador, J. P., "Simulation of a 250kW Diesel Fuel Processor/ PEM Fuel Cell System," *J. Power Sources* 71 (1998) 179.
22. Voss, H. and Huff, J., "Portable Fuel Cell Power Generator," *J. Power Sources* 65 (1997) 155.
23. Palo, D. P., Holladay, J. D., Rozmiarek, R. T., Guzman-Leong, C. E., Wang, Y., Hu, J., Chin, Y-H., Dagle, R. A. and Baker E. G., "Development of a Soldier-Portable Fuel Cell Power System Part I: A Bread-Board Methanol Fuel Processor," *J. Power Sources* 108 (2002)28.
24. Wohllwend, K., Maurice, L. Q. and Edwards, T., "Thermal Stability of Energetic Hydrocarbon Fuels for Use in Combined Cycle Engines," *J. Propulsion and Power* 17 (2001) 1258.
25. Baumert, R. M., Epp, D. G. and Peters, E. J., "Radial Flow Fuel Processor," US Patent 5,676,911 (1997).
26. Rogers, S., Gervasio, D., Koripella, R., Samms, S., and Tasic, S., "Multi-Layered Ceramic Fuel Cell System Based on Steam Reforming Methanol to H₂-Enriched Gas," *Proc. 40th Power Sources Conference* (2002) 269.
27. Ahmed, S. and Krumpelt, M., "Hydrogen from Hydrocarbon Fuels for Fuel Cells," *International Journal of Hydrogen Energy* 26 (2001) 291.

28. Edwards, N, Frost, J. S., Jones, A. and Pignon, J. F., "Self-Sustaining Hydrogen Generator," US Patent 5,762,658 (1998).
29. Docter, A. and Lamm, A., "Gasoline Fuel Cell Systems," *J. Power Sources* 84 (1999) 194.
30. Clawson, L. G., Mitchell, W. L., Bentley, J. M. B. and Thijssen, J. H. J., "Method and Apparatus for Converting Hydrocarbon Fuel into Hydrogen Gas and Carbon Dioxide," US Patent 6,126,908 (2000).
31. Farrauto, R. et al. AIChE Spring conference, New Orleans (2002).
32. Pettersson, L. J. and Westerholm, R., "State of the Art of Multi-fuel Reformers for Fuel Cell Vehicles: Problem Identification and Research Needs," *Int. J. of Hydrogen Energy* 26 (2001) 243.
33. Schuessler, M., Lamla, O., Stefanovski, T., Klein, C. and zur Megede, D., "Autothermal Reforming of Methanol in a Isothermal Reactor-Concept and Realisation," *Chem. Eng. Technol.* 24 (2001) 11.
34. Buxbaum, R. B., "Membrane Reactor Advantages for Methanol and Similar Reactions," *Separation Science and Technology* 34 (1999) 2113.
35. Wieland, S., Melin, S. and Lamm, A., "Membrane Reactors for Hydrogen Production," *Chemical Engineering Science* 57 (2002) 1571.
36. Zalc, J. M., Sokolovskii, V. and Loffler, D. G., "Are Noble Metal-Based Water-Gas Shift Catalysts Practical for Automotive Fuel Processing?" *J. Catalysis* 206 (2002) 169.
37. Heck, R. M. and Farrauto, *Catalytic Air Pollution Control: Commercial Technology*, 2nd Edition Wiley, New York (2002).
38. Twigg, M. V. and Spencer, M. S., "Deactivation of Supported Copper Metal Catalysts for Hydrogenation Reactions," *Applied Catalysis A: General* 212 (2001) 161.
39. http://www.fuelcellmaterials.com/water_gas_shift_catalysts.htm, viewed on 7/26/02.
40. Bunluesin, T., Gorte, R. J., Graham, G. W., "Studies of the Water-Gas-Shift Reaction on Ceria-Supported Pt, Pd, and Rh: Implications for Oxygen-Storage Properties," *Applied Catalysis B: Environmental* 15 (1998) 107.
41. Hilaire, S., Wang, X., Luo, T., Gorte, R. J. and Wagner, J., "A Comparative Study of Water-Gas-Shift Reaction over Ceria Supported Metallic Catalysts," *Applied Catalysis A: General* 215 (2001) 271.
42. Li, Y., Fu, Q. and Flytzani-Stephanopoulos, M., "Low-Temperature Water-Gas Shift Reaction over Cu- and Ni-loaded Cerium Oxide Catalysts," *Applied Catalysis B: Environmental* 27 (2000) 179.
43. Low-Temperature Water-Gas Shift," *Catalysis Letters* 77 (2001) 87.
44. Andreeva, D., Idakiev, V., Tabakova, T., Ilieva, L., Falaras, P., Bourlinos, A., Travlos, A., "Low Temperature Water-Gas Shift Reaction over Au/CeO₂ Catalysts," *Catalysis Today* 72 (2002) 51.

45. Bond, G. C. and Thompson, D. T., "Catalysis by Gold," *Catal. Rev. – Sci. Eng.* 41 (1999) 319.
46. Tabakova, T., Idakiev, V., Andreeva, D. and Mitov, I., "Influence of the Microscopic Properties of the Support on the Catalytic Activity of Au/ZnO, Au/ZrO₂, Au/Fe₂O₃, Au/Fe₂O₃-ZnO, Au/Fe₂O₃-ZrO₂ Catalysts for the WGS Reaction," *Applied Catalysis A: General* 202 (2000) 91.
47. Boccuzzi, F., Chiorino, A., Manzoli, M., Andreeva, D., Tabakova, T., Ilieva, L. and Iadakev, V., "Gold, Silver and Copper Catalysts Supported on TiO₂ for Pure Hydrogen Production," *Catalysis Today* 75 (2002) 169.
48. Sanchez, J. G. and Tsotsis, T. T., *Catalytic Membranes & Catalytic Membrane Reactors*, VCH Verlagsgesellschaft MbH, (2002).
49. Shu, J., Grandjean, B. P. A., Vanneste, A. and Kaliaguine, S., "Catalytic Palladium-Based Membrane Reactors-A Review," *Canadian Journal of Chemical Engineering* 69 (1991) 1036
50. Coronas, J. and Santamaria, J., "Catalytic Reactors Based on Porous Membranes," *Catal. Today* 25 (1999) 377.
51. Julbe, A., Farrusseng, D., Guizard, C., "Porous Ceramic Membranes for Catalytic Reactors - Overview and New Ideas," *J. Membrane Science* 181 (2001) 3.
52. Armor, J. N., "Applications of Catalytic Inorganic Membrane Reactors to Refinery Products," *J. Membrane Science* 147 (1998) 217.
53. Edlund, D. J., Newbold, D. D. and Frost, C. B., "Composite Hydrogen Separation Element and Module," US Patent 5,645,626 (1997).
54. Buxbaum, R. E., "Composite Metal Membrane for Hydrogen Extraction," US Patent 5,215,729 (1993).
55. Criscuoli, A., Basile, A. and Drioli, E., "An Analysis of the Performance of Membrane Reactors for the Water-Gas Shift Reaction using Gas Feed Mixtures," *Catalysis Today* 56 (2000) 53.
56. Armor, J. N., "The Multiple Roles for Catalysis in the Production of H₂," *Applied Catalysis A: General* 176 (1999) 159.
57. Li, A., Liang, W. and Hughes, R., "The Effect of Carbon Monoxide and Steam on the Hydrogen Permeability of a Pd/Stainless Steel Membrane," *J. Membrane Science* 165 (2000) 135.
58. Antoniazzi, A. B., Haasz, A. A. and Stangeby, P. C., "The Effect of Adsorbed Carbon and Sulfur on Hydrogen Permeation through Palladium," *J. Nuclear Materials* 162 (1989) 1065.
59. Peden, C. H., Kay, B. D. and Goodman, D. W., "Kinetics of Hydrogen Adsorption by Chemically Modified Pd(110)," *Surface Science* 175 (1986) 215.
60. Borup, R. L., Skala, G. w., Brundage, M. A. and LaBarge, W. J., "Method and Apparatus for Selective Removal of Carbon Monoxide," US Patent 6,162,558 (2000).

61. Korotkikh, O. and Farrauto, R., "Selective Catalytic Oxidation of CO in H₂: Fuel Cell Applications," *Catalysis Today* 62 (2000) 249.
62. Liu, X., Korotkikh, O. and Farrauto, R., "Selective Catalytic Oxidation of CO in H₂: Structural Study of Fe Oxide-Promoted Pt/Alumina Catalyst," *Applied Catalysis A: General* 226 (2002) 293.
63. Igarashi, H., Uchida, H., Suzuki, M., Sasaki, Y. and Watanabe, M., "Removal of Carbon Monoxide from Hydrogen-Rich Fuels by Selective Oxidation over Platinum Catalyst Supported on Zeolite," *Applied Catalysis A: General* 159 (1997) 159.
64. Manasilp, A. and Gulari, E., "Selective CO oxidation over Pt/Alumina Catalysts for Fuel Cell Applications," *Applied Catalysis B: Environmental* 37 (2002) 17.
65. zur Megede, D., "Fuel Processors for Fuel Cell Vehicles," *J. Power Sources* 106 (2002) 35.
66. Vanderborgh, N. E., Springer, T. E. and Huff, J. R., "Fuel Processor for Fuel-Cell Power System," US Patent 4,650,727 (1987).
67. James, B. D., "Fuel Reformer System for a Fuel Cell," US Patent 6,329,091 (2001).
68. Lomax, F. D. and Ijaz, M. I., "Fuel Cell Power Generation System and Method for Powering an Electric Vehicle," US Patent 6,368,735 (2002).
69. Emonts, B., Bogild Hansen, J., Schmidt, H., Grube, T., Hohlein, B., Peters, R. and Tschauder, A., "Fuel Cell Drive System with Hydrogen Generation in Test," *J. Power Sources* 86 (2000) 228.
70. Okamoto, T., "Method for Supplying Fuel Gas to Fuel Cell Assembly," US Patent 5,714,276.
71. Skala, G. W., Hart-Predmore, D. J., Pettit, W. H. and Borup, R. L., "Thermally Integrated Staged Methanol Reformer and Method," US Patent 6,238,815 (2001).
72. Autenrieth, R. and Heil, D., "Reforming Reactor, Particularly for the Water Vapor Reforming of Methanol," US Patent 5,928,614 (1999).
73. Brown, L. F., "A Comparative Study of Fuels for On-Board Hydrogen Production for Fuel-Cell-Powered Automobile," *International Journal of Hydrogen Power* 26 (2001) 381.
74. Cable, T. L.; Brakas, A. B.; Ruhl, R. C. and Milliken, C. E. "Method for Steam Reforming Hydrocarbons using a Sulfur-Tolerant Catalyst," US Patent 6,238,816 (2001).
75. Trimm, D. L., "Catalysts for the Control of Coking during Steam Reforming," *Catalysis Today* 49 (1999) 3.
76. Rostrup-Nielsen, J. R. and Alstrup, I., "Innovation and Science in the Process Industry Steam Reforming and Hydrogenolysis," *Catalysis Today* 53 (1999) 311.
77. Palm, C., Cremer, P., Peters, R. and Stolten, D., "Small-Scale Testing of a Precious Metal Catalyst in the Autothermal Reforming of Various Hydrocarbon Feeds," *J. Power Sources* 106 (2002) 231.

78. Kobayashi, M and Flytzani-Stephanopoulos, M., "Reduction and Sulfidation Kinetics of Cerium Oxide and Cu-Modified Cerium Oxide," submitted.
79. Arakawa, H., Aresta, M., armor, J. N., Barteau, M. A., Beckman, E. J., Bell, T. T., Bercaw, J. E., Creutz, C., Dinjus, E., Dixon, D. A., Domen, K., DuBois, D. L., Eckert, J., Fujita, E., Gibson, D. H., Goddard, W. A., Goodman, D. W., Keller, J., Kubas, G. J., Kung, H. H., Lyons, J. E., Manzer, L. E., Marks, T. J., Morokuma, K., Nicholas, K. M., Periana, R., Que, L., Rostrup-Nielson, J., Sachtler, W. M. H., Schmidt, L. D., Sen, A., Somorjai, G. A., Stair, P. C., Stults, B. R. and Tumas, W., "Catalysis Research Relevance to Carbon Management: Progress, Challenges, and Opportunities," *Chem. Rev.* 101 (2001) 953.
80. World Bank Report on Pakistan Clean Fuels: October 2001,
http://www.worldbank.org/html/fpd/esmap/pdfs/pakistan_cleanfuels.pdf, viewed on 7/11/02.
81. EPA, "Control of Air Pollution from New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements," *Federal Register* 66 (2001) 5002.
82. Franz, N., "Court Upholds Sulfur Limits for Diesel," *Chemical Week* 164 (2002) 38.
83. "Standard Specification for Diesel Fuel Oils," ASTM D975-02.
84. Ma, X., Sakanishi, K. and Mochida, I., "Hydrodesulfurization Reactivities of Various Sulfur Compounds in Diesel Fuel," *Ind. Eng. Chem. Res.* 33 (1994) 218.
85. Gates, B. C. and Topsøe, H., "Reactivities in Deep Hydrodesulfurization: Challenges, Opportunities, and the Importance of 4-Methyldibenzothiophene and 4,6-Dimethyldibenzothiophene," *Polyhedron* 16 (1997) 3213.
86. Lee, S. H. D., Kumar, R. and Krumpelt, M., "Sulfur Removal from Diesel Fuel-Contaminated Methanol," *Separation and Purification Technology* 26 (2002) 247.
87. Khan, A. R., Meek, J. and Baker, B. S., "Jet Fuel as a Feedstock," *Chemical Engineering Progress* 62 (1966) 74.
88. Anumakonda, A., Yamanis, J. and Ferrall, J., "Catalytic Partial Oxidation of Hydrocarbon Fuels to Hydrogen and Carbon Monoxide," US Patent 6,221,280 (2001).
89. MSDS for 100% Methanol, www.alfa.com.
90. MSDS for ARCO Emission Control Diesel #2, www.ecdiesel.com.
91. MSDS for JP-8, www.caltex.com.
92. Amphlett, J. C., Mann, R. F. and Peppley, B. A., "On Board Hydrogen Purification for Steam Reformation / PEM Fuel Vehicle Power Plants," *Int. J. Hydrogen Energy* 21 (1996) 673.

Appendix A. Chemical and Physical Properties of Methanol, Diesel, and JP-8

Table A-1. Selected chemical properties for methanol, JP-8, and diesel

| | Methanol [89] | Diesel [90] | JP-8 [24,91] |
|-------------------------|--------------------|---|--|
| Molecular Formula | CH ₃ OH | Mixture of Compounds, C _{13.57} H _{27.14} [73] | Mixture of Compounds, C _{10.9} H _{20.9} |
| Energy Density (LHV), | 5.6 | 11.1 | 11.8 |
| Molecular Weight | 32 | 190 [73] | 152 |
| Density | 0.79 (20 °C) | 0.81 to 0.84 | 0.8 |
| Vapor Pressure | 129 hPa (20 °C) | 0.04 Reid Psia (100°F) | < 7 mmHg (25 °C) |
| Explosion Limits, vol% | 6.7 – 36 | 0.7 – 5.0 | 0.6 - 4.5 |
| Boiling Point, K | 338 | 450–643 | 448-543 |
| Flash Point, K | 284 | 344–371 | 311 |
| Ignition Temperature, K | 658 | 530 | 653 |

INTENTIONALLY LEFT BLANK.